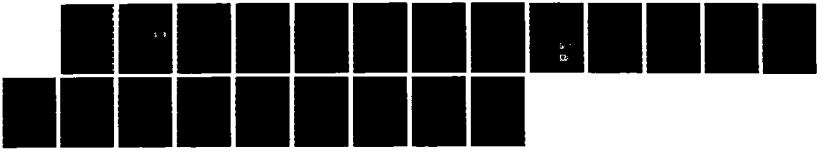
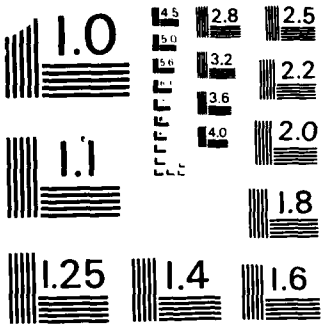
AD-A169 487 TEMPERATURE COMPENSATION IN THE '2:17' TYPE MAGNETS(U) 1/1
CRUCIBLE MATERIALS CORP PITTSBURGH PA CRUCIBLE RESEARCH
CENTER K S NARASIMHAN ET AL. MAR 86 ARO-19511.3-MS
UNCLASSIFIED DAAG29-83-C-0007 F/G 20/3 NL





MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS - 1963 - A

AD-A169 487

ARO 19511.3-MS

(2)

TEMPERATURE COMPENSATION IN THE '2:17' TYPE MAGNETS

FINAL REPORT

K. S. V. L. Narasimhan, F. E. Camp,
Bao-Min Ma, C. J. Willman

MARCH 1986

DTIC
ELECTE
JUN 26 1986
S D
D

U. S. ARMY RESEARCH OFFICE

Contract - DAAG29-83-C-0007

CRUCIBLE MATERIALS CORPORATION
CRUCIBLE RESEARCH CENTER
PITTSBURGH, PA.

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED.

DTIC FILE COPY

THE VIEW, OPINIONS, AND/OR FINDINGS CONTAINED IN THIS REPORT ARE THOSE OF THE AUTHOR(S) AND SHOULD NOT BE CONSTRUED AS AN OFFICIAL DEPARTMENT OF THE ARMY POSITION, POLICY, OR DECISION, UNLESS SO DESIGNATED BY OTHER DOCUMENTATION.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ARO 19511.3-MS	2. GOVT ACCESSION NO. N/A	3. RECIPIENT'S CATALOG NUMBER N/A
4. TITLE (and Subtitle) Temperature Compensation in the '2:17' Type Magnets		5. TYPE OF REPORT & PERIOD COVERED Final Report Jan. 1983 - Dec. 1985
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) K. S. V. L. Narasimhan, F. E. Camp, Bao-Min Ma, C. J. Willman		8. CONTRACT OR GRANT NUMBER(s) DAAG29-83-C-0007
9. PERFORMING ORGANIZATION NAME AND ADDRESS Crucible Materials Corporation Crucible Research Center P. O. Box 88, Pittsburgh, Pa. 15230		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		12. REPORT DATE March 1986
		13. NUMBER OF PAGES 17
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

NA

18. SUPPLEMENTARY NOTES

The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Magnets, Travelling Wave Tubes, Temperature Compensation, Sm-Co, Pr-Co, Nd-Co, NdFeB.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Development of temperature compensated magnets was undertaken in both '2:17' and NdFeB type of alloys. A number of alloys have been identified that can produce energy product in excess of 40 MGOe in the uncompensated material. Computer programs were developed for identifying key compositions that were then processed successfully into temperature compensated magnets. Current materials can produce temperature compensated magnets with an energy product not exceeding 22 MGOe. Further work is necessary to develop temperature compensated magnets with an energy product exceeding 30 MGOe.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Proposal Number 19511-MS
Funding Document DAAG29-83-C-0007

Temperature Compensation in the '2:17' Type Magnets

Pr and Nd Substituted '2:17' Magnets for Elevated Temperature Application

The program was conducted in three phases. Phase I dealt with identifying composition ranges between RCo_5-R_2Co_{17} that can produce maximum induction. Anisotropy field and saturation magnetization were measured on a series of Sm, Pr, and Nd alloys. The results indicate that Pr, Nd or a combination of both can be effectively utilized for increasing the saturation induction and yet maintain reasonable values of anisotropy field. Energy products greater than 40 MGOe are possible.

Phase II addressed the issue of temperature compensation in the '2:17' type of magnets to permit the utilization of these magnets in travelling wave tubes operating at 200-250°C. A computer assisted composition selection procedure was adopted that allowed pinpointing compositions that will yield best temperature compensation. Magnets fabricated from the identified compositions produced temperature coefficient that satisfied the program goals (+0.0008% per °C over a temperature range of -50 to room temperature and -0.007% per °C over room temperature to 250°C).

Phase III dealt with developing temperature compensation in the NdFeB type of alloys. Nearly 3000 compositions were generated through the computer. Combinations of light rare earth with heavy, heavy rare earth-with heavy and two heavy rare earth with light rare earth were examined. Two compositions were chosen and processed into magnets.

Listed below are their composition, magnetic properties, and temperature coefficients.

Magnet #1: $(Nd_{0.24}Ho_{0.70}Er_{0.06})_{15}Fe_{79}B_6$, ATC-112 + 24% Alloy #6

B_r = 7,900 Gauss
H_c = 7,700 Oe
H_{ci} = 14,400 Oe
BH_{max} = 15.2 MGOe
H_k = 13,000 Oe
Density = 7.8 gm/cc

Temperature Range (°C)	Temperature Coefficient α (% per °C)
-50 to +150	-0.0345 (-0.013 predicted)
-50 to +25	+0.0081
+25 to +100	-0.0399

Magnet #2: $(Nd_{0.24}Ho_{0.64}Dy_{0.13})_{15}Fe_{79}B_6$, ATC-110 + 18% Alloy #4

B_r = 7,700 Gauss
H_c = 7,700 Oe
H_{ci} = 20,600 Oe
BH_{max} = 14.8 MGOe
H_k = 18,300 Oe
Density = 7.98 gm/cc

Temperature Range (°C)	Temperature Coefficient α (% per °C)
-50 to +150	-0.0299 (-0.012 predicted)
-50 to +75	-0.0033
-25 to +75	-0.0066
-50 to 0	+0.0152

QUALITY INSPECTED 3
Codes
and/or
Special
A-1

IEEE TRANSACTIONS ON MAGNETICS,
VOL. MAG-21, NO. 5, SEPTEMBER 1985

TEMPERATURE COMPENSATION IN THE '2:17' TYPE MAGNETS

F. E. Camp, K. S. V. L. Narasimhan, and J. C. Hurt

ABSTRACT

Compensation for the temperature dependence of magnetic flux has been investigated in the '2:17' type permanent magnet alloys. A computer assisted composition selection procedure was adapted and one of the identified compositions, $Sm_{1.18}Dy_{.81}Gd_{.01}Co_{9.76}Fe_{4.19}Cu_{.83}Zr_{.34}$, was processed into magnets. The measured temperature coefficients correlated satisfactorily with the prediction. Dysprosium was found to be a better substituent for Sm than either Gd or Er in providing temperature coefficient of linearity.

INTRODUCTION

Temperature compensated magnets have found application in devices such as gyros, accelerometers, and to a certain extent, in travelling wave tubes. Samarium cobalt magnets have been successfully temperature compensated by alloying with heavy rare earths[1-4]. For a fully compensated $SmCo_5$ magnet, the maximum energy product attainable is 7.0 MGOe[5]. Further miniaturization of devices is possible only if the BH_{max} is increased further to possibly 16-20 MGOe. We have investigated rare earth-cobalt '2:17' type of alloys to improve the BH_{max} of a fully compensated magnet.

Temperature compensation in '2:17' type alloys has been investigated by various authors[6,7]. However, a generalized approach for identifying the alloys that can provide the needed temperature coefficient has not been made. Such an approach is necessary to permit alloy development suited to the need of a particular device since the flux in the gap is dependent not only on the characteristics of the magnet but also on the temperature variation of the device gap. This publication presents an analytical approach to composition selection and the results on an alloy from this selection.

EXPERIMENTAL

The molar composition of the base alloy was $Sm_2Co_{9.76}Fe_{4.19}Cu_{.83}Zr_{.34}$ (Sm_2TM_{15}). This and four heavy rare earth analogs, $SmDyTM_{15}$, $SmErTM_{15}$, $SmGdTM_{15}$, and $SmHoTM_{15}$ were each induction melted under argon gas and cast into split copper molds. The ingots were crushed to 75μm powder and thermomagnetic measurements made over the temperature range of -60°C to 220°C. The Faraday technique was used with an applied field of 5 kilo-oersteds.

The composition that was predicted to have the smallest temperature coefficients was $Sm_{1.18}Dy_{.81}Gd_{.01}TM_{15}$. It was induction melted by the above procedure and pulverized to -60 mesh powder. Jet milling with argon gas produced an average particle size of ~5 microns. The base alloy, Sm_2TM_{15}, was also jet milled to ~5 microns. Magnets (1cm diameter x 7cm long) were pressed, sintered between 1150-1200°C for 1 hour, solutionized for 5 hours between 1120-1160°C, then quenched. They were then further heat treated at 800-850°C and slowly cooled to 400°C then naturally cooled to room temperature.

Camp and Narasimhan are with Colt Industries, Crucible Research Center, Pittsburgh, PA 15230, and Hurt is with the Army Research Office, Research Triangle Park, NC 27709.

After hysteresis loops were determined for centerless ground and cut samples, temperature coefficients of magnetization were measured with an oscillating sample magnetometer. The magnetized sample (0.75cm diameter x 3cm long) and the pick-up coil were positioned within a cooling/heating environmental chamber. When thermal equilibrium was reached, the sample was driven through the coil at a constant speed. The magnetic flux so generated was measured and integrated over the length with a 6.5 digit voltmeter input to a desk computer.

RESULTS AND DISCUSSION

The thermomagnetic data determined by the Faraday technique are shown in Figure 1. The base alloy has a large negative temperature coefficient of magnetization over the entire temperature range, while the curves for the alloys containing Dy, Er, Gd, or Ho show less variation and have positive temperature coefficients in their cooler regions. This phenomenon, which is typical of heavy and light rare earth-transition metal (Fe, Co) alloys of the 1:5 and 2:17 stoichiometry, suggests a method of approaching temperature independence of magnetization with the judicious selection of heavy rare earth combinations and concentrations.

We have generated a number of theoretical magnetization curves from these experimental data. A simplifying assumption was made that, at a given temperature, magnetization is an additive property with the number of rare earth atoms. Implicit in this assumption is that crystal field effects are unchanged by the addition of heavy rare earths.

Incremental interpolations were calculated between the base alloy and each heavy rare earth analog. These interpolations resulted in families of curves or data arrays for each heavy rare earth. A large number of magnetization vs temperature curves were then computer generated from these data arrays. Various concentrations of either two, three, or all four heavy rare earths were considered.

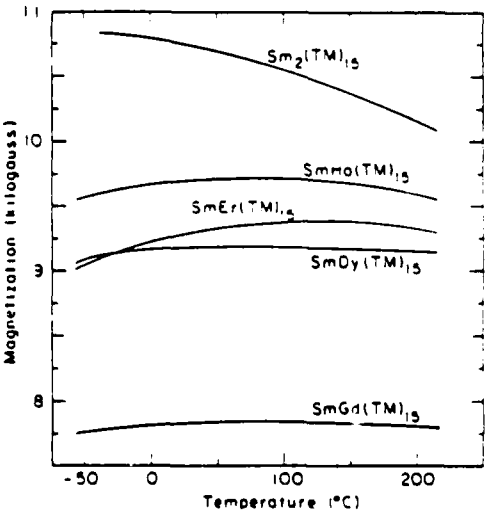


Figure 1. Magnetization vs temperature data measured for the Sm and heavy rare earth substituted for Sm alloys. TM=$Co_{9.76}Fe_{4.19}Cu_{.83}Zr_{.34}$

Due to space limitations, we have selected certain families of curves for inclusion here on the basis of two criteria--those showing the greater linearity, and others displaying the effects of all the heavy rare earths considered. Figures 2, 3, 4 and 5 show the hypothetical curves for two heavy rare earth additives. The formulations predicting the lowest temperature coefficients are shown on these figures and are listed in Table I. The coefficients were calculated by the least squares method.

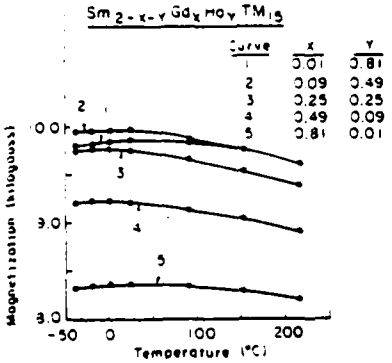


Figure 2. Computer generated curves for the Gd and Ho substituted alloys.

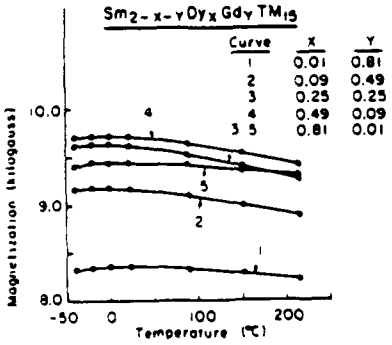


Figure 3. Computer generated curves for the Dy and Gd substituted alloys.

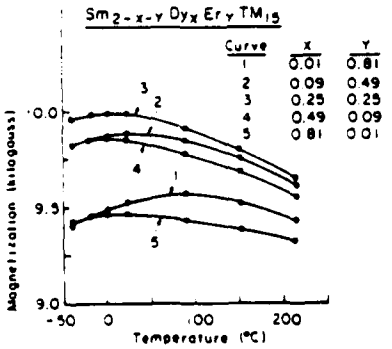


Figure 4. Computer generated curves for the Dy and Er substituted alloys.

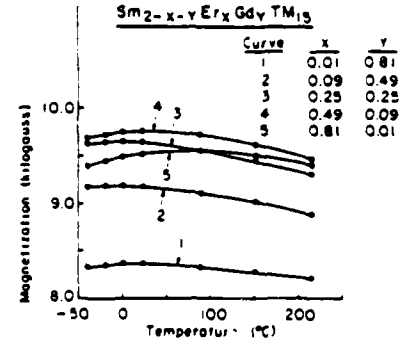


Figure 5. Computer generated curves for the Er and Gd substituted alloys.

Table I. Alloys with Predicted Low Temperature Coefficients of Magnetization

Alloy	Temperature Coefficient, $\%^{\circ}C^{-1}$ -50 to 25°C	25°C to 250°C
$Sm_{1.18}Dy_{.81}Gd_{.01}TM_{15}$	+.00624	-.00788
$Sm_{1.18}Gd_{.81}Ho_{.01}TM_{15}$	+.00713	-.00793
$Sm_{1.42}Er_{.09}Gd_{.49}TM_{15}$	+.00298	-.0164
$Sm_{1.18}Gd_{.81}Dy_{.01}TM_{15}$	+.00705	-.00901
$Sm_{1.18}Ho_{.81}Gd_{.01}TM_{15}$	+.012	-.0121

Figures 6 and 7 show typical curves for three heavy rare earth components, and Figure 8 contains some curves for all four heavy rare earths. There is less linearity exhibited in these multi-component predictions than was evident in the two component results.

The alloy predicted to have the lowest temperature coefficient, $Sm_{1.18}Dy_{.81}Gd_{.09}TM_{15}$, was prepared and fabricated into a magnet. The following magnetic properties were measured: B_r=8,900 Gauss, H_{ci}=7,750 Oersted, H_c=6,300 Oersted, and BH_{max}=16.5 MGOe. The results of temperature coefficient measurements are shown in Figure 9 along with the predicted curve for this alloy. Although the experimental curve lies below the predicted curve (absolute magnetization values smaller by 5%), there is good agreement between the shapes of the curves and their respective slopes. The low temperature coefficients are $+.0008\%^{\circ}C^{-1}$(experimental) versus $+.00624\%^{\circ}C^{-1}$(predicted). The other set of coefficients is $-.00774\%^{\circ}C^{-1}$(experimental) and $-.00788\%^{\circ}C^{-1}$(predicted). This is indicative of the validity of this procedure to predict the general shape of magnetization versus temperature curves for various alloys incorporating heavy rare earths for temperature compensation.

Previous work has shown the temperature compensation benefits of Gd[8] and Er[7], with which we concur. The former has the disadvantage of lowering magnetization values more so than others. We have shown that Dy is also an excellent candidate. It will provide linearity over a broader temperature range than Er does. This is graphically displayed by comparing curves 1 and 5 in Figure 4, where the higher Dy content (Curve 5) shows less variation over the -50°C to 222°C temperature range than the corresponding Er curve.

It is also displayed by noting the difference in curve shapes between Figures 6 and 7, where Dy and Er, respectively, are dominant in otherwise identical ternary heavy rare earth systems. Dy has an additional economic advantage as being the least expensive of the four heavy rare earths considered.

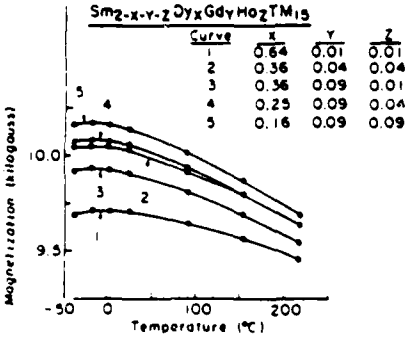


Figure 6. Computer generated curves for three component rare earth alloys.

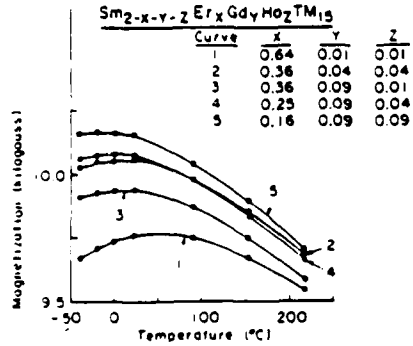


Figure 7. Computer generated curves for three component rare earth alloys.

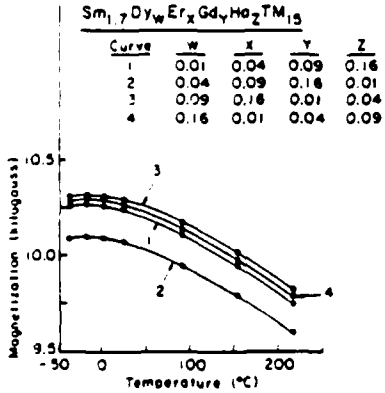


Figure 8. Computer generated curves for four component rare earth alloys.

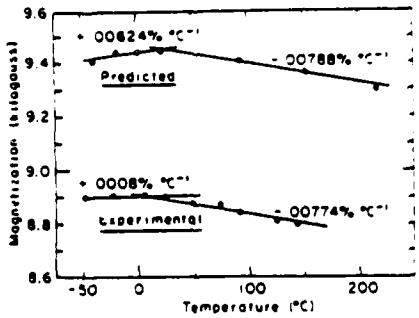


Figure 9. Experimental and predicted temperature dependence of magnetization data for $Sm_{1.18}Dy_{.81}Gd_{.01}TM_{15}$ alloy. The numbers on the curves refer to the temperature coefficient of magnetization over the low (-50° to 0°C) and high temperatures (0° to 250°C).

CONCLUSIONS

The proposed method of predicting the behavior of heavy rare earth additions to alloy systems may be used in place of the "trial and error" procedures. Dy additions result in improved temperature compensation over a broad temperature range. Gd is effective over the same range, but significantly lowers the magnetization. Erbium will give results similar to Dy, but over a smaller temperature range. Dy has the added advantage of being the least expensive.

Acknowledgments

We thank E. J. Dulis for his interest in this work and M. Quinn for his help in the earlier part of the program.

This work was supported by a grant from Army Research Office Contract No. DAA629-83-C-007.

REFERENCES

1. M. G. Benz, R. P. Laforce and D. L. Martin, AIP Conf. Proc., No. 18, 1173 (1974).
2. F. G. Jones and M. Tokunaga, IEEE Trans. Magn., Vol. MAG-12, 968 (1976).
3. K. S. V. L. Narasimhan, M. G. H. Wells and D. V. Ratnam, J. App. Physics, 49, 2072, (1978).
4. K. S. V. L. Narasimhan, J. App. Physics, Vol. 52, No. 3, 2512 (1980).
5. K. S. V. L. Narasimhan, Fifth International Workshop on Rare Earth-Cobalt Permanent Magnets and Applications, Roanoke, Va., June 1981, University of Dayton, 629 (1981).
6. F. Rothwarf, H. A. Leupold, A. Tauber, J. T. Breslin, R. L. Bergner and J. J. Winter, The Rare Earths in Modern Science and Technology, Vol. 2, edited by G. J. McCarthy, J. J. Rhyne and H. B. Siber (Plenum, New York 1980).
7. H. F. Mildrum, J. B. Krupar and A. E. Ray, J. Less-Common Met. 93, 261 (1983).
8. R. L. Bergner, H. A. Leupold, J. T. Breslin, F. Rothwarf and A. Tauber, J. App. Physics, 50, 2349, (1979).

The material contained in this paper is intended for general information only and should not be used in relation to any specific application without independent study and determination of its applicability and suitability for the intended application. Anyone making use of this material or relying thereon, assumes all risk and liability therefrom.

IEEE TRANSACTIONS ON MAGNETICS,
VOL. MAG-21, NO. 5, SEPTEMBER 1985

Pr AND Nd SUBSTITUTED '2:17' MAGNETS FOR ELEVATED TEMPERATURE APPLICATION

C. J. Willman and K. S. V. L. Narasimhan

ABSTRACT

Results of Pr, Nd and (PrNd) substitution in the '2:17' type permanent magnet alloys are presented. Microstructural studies, crystal structure, anisotropy field (H_A), Curie temperature (T_C), and saturation magnetization (M_S) were used as tools for the evaluation of these alloys. Pr, Nd and (PrNd) increases M_S without significantly affecting the T_C. H_A decreases when Sm is replaced by Pr, Nd or (PrNd). Several of the alloys investigated show promise to be permanent magnets.

INTRODUCTION

'2:17' type of permanent magnets have been in production for the last several years. The general stoichiometry is about $RM_{7.4-7.7}$ where M is a combination of Fe, Co, Cu, Zr[1-3]. The maximum energy product attainable is 33 MGOe[2]. Further increase in the BH_{max} is possible if the saturation magnetization (M_S) is increased by increasing the number of moment carrying atoms, i.e., Fe and Co. Samarium has a very small magnetic moment to contribute. Shimoda et al[3] and Ray et al[4] have increased the M value from 7.4 to 8.35 by increasing the iron content and successfully made magnets. The M_S value reported was 11,500 - 11,800 Gauss. The maximum energy product attainable is 33-35 MGOe assuming the anisotropy field is high and BH_{max} can be approximated to $B_r^2/4$. The increase in iron content alone is not able to increase the saturation magnetization past 12,000 Gauss. It is possible to increase the induction by decreasing the copper content since copper acts as a diluent for the magnetic moment. However, copper is vital for the generation of coercive force and hence cannot be reduced significantly. We, therefore, added Pr and Nd to increase the saturation induction and the results of these investigations are presented in this paper.

EXPERIMENTAL PROCEDURE

The alloys were prepared by induction melting the elements and casting the alloy into a copper mold.

1. X-ray Data: X-ray diffraction data was obtained using a Norelco X-ray Generator (40kV, 12mA) in conjunction with a 114.7 Debye Scherrer camera. CrKa radiation was used on -100 mesh alloy powder. The resulting powder patterns were indexed. An iterative least squares technique was used to calculate the lattice parameters of each alloy.

2. Curie Temperature Evaluation: Homogenized alloy was crushed to -100 mesh and TMA (thermomagnetic analysis) was used to determine T_C and other magnetic phases. A field of 1 kOe was used for this study.

3. Saturation Magnetization: Homogenized alloy was crushed and ground to -400 mesh in argon. Aliquots of 50-80 mg were measured into the VSM (vibrating sample magnetometer) holder. The VSM was calibrated with a Ni standard using σ_{Ni} = 54.40 emu/g at 295K. Honda plots were extrapolated to obtain σ saturation.

4. Anisotropy Field: Alloy was crushed to -325 mesh. The powder was then dispersed in paraffin wax and aligned in a 25 kOe field and allowed to harden in the presence of a field. The field required to saturate in the direction parallel and perpendicular to the easy direction were evaluated. H_A was determined as the field required to saturate the material in the perpendicular direction.

DISCUSSION

The X-ray diffraction patterns of the alloys studied could be indexed to a Th_2Ni_{17} (hexagonal) type structure. This structure is characteristic of high-temperature, disordered Sm_2Co_{17}[5]. The as-cast alloys were 2-phase. With increased Fe substitution for Co and with rare earth substitutions for Sm, more complex microstructures were observed. Homogenization of the as-cast structure was possible between 1165-1185°C for most alloys (see Figures 1 through 3). Those alloys having complex microstructures were more difficult to homogenize.

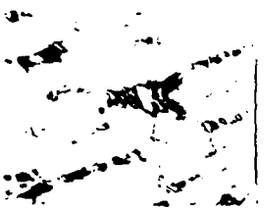


Figure 1a 125X
*x=0, v=0.2
Prior to Heat Treatment

Figure 1b 125X
*x=0, v=0.2
After Heat Treatment

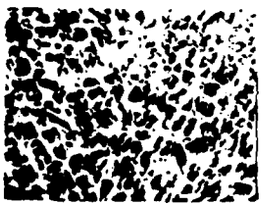


Figure 2a 125X
*RE=Nd, x=0.1, v=0.2
Prior to Heat Treatment

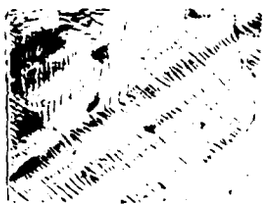


Figure 2b 125X
*RE=Nd, x=0.1, v=0.2
After Heat Treatment

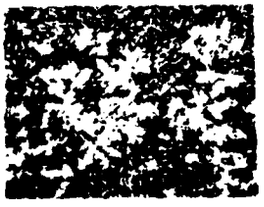


Figure 3a 125X
*RE=Nd, x=0.3, v=0.4
Prior to Heat Treatment

Figure 3b 125X
*RE=Nd, x=0.3, v=0.4
After Heat Treatment

$^*Sm_{1-x}RE^*_x Co_{7.90-v}Fe_{0.10}Cu_{0.08}Zr_{0.02}$ 8.35

Willman and Narasimhan are with Colt Industries, Crucible Research Center, Pittsburgh, PA 15230.

Most secondary phases were able to be solutionized with the exception of a white phase. This phase was determined to be an Fe-Co rich phase. The presence of this phase was particularly prominent in those alloys (as-cast condition) having the largest substitutions of Fe for Co (y=0.3, 0.4).

Figures 4 and 5 illustrate the magnetization vs temperature plots obtained for these alloys. As expected, Fe substitution for Co was found to decrease the Curie temperature. Pr, Nd, 50%Pr-50%Nd substitution for Sm did not affect the Curie temperature significantly.

The saturation magnetization of these alloys increases with increasing Fe, Pr, Nd, or Pr/Nd substitutions. Some of the alloy samples were exceptionally difficult to saturate and consequently M_S was more difficult to measure.

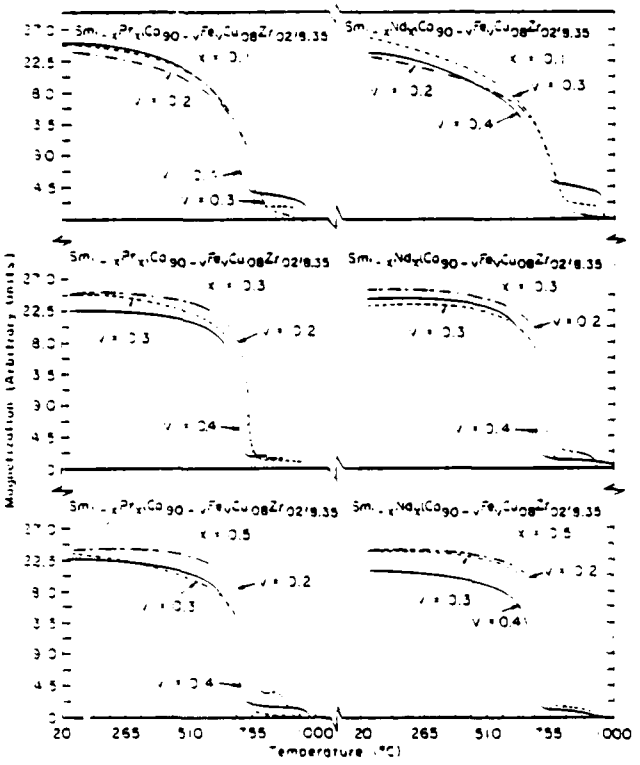


Figure 4. Temperature dependence of magnetization at an applied field of 1 kOe.

Table I illustrates the magnetization observed at an applied field of 18 kG, and the value of the magnetization extrapolated to infinite field. Calculation of the theoretical BH_{max} ($B_S^2/4$) is also included in Table I.

The substitution of Pr, Nd, Pr/Nd for Sm in most cases decreased the anisotropy field, H_A. Fe substitution for Co usually decreased the anisotropy field. The effect of these substitutions is illustrated in Figures 6 and 7. Nd and Pr in the '2:17' alloys prefer a basal plane[6] and substitution of these elements reduces the overall preference of the rare earth sublattice to the magnetically easy C-direction, hence a decreased anisotropy field. The preference of iron sublattice in the '2:17' alloy is in the basal phase and the effect of iron substitution is also to decrease the anisotropy field.

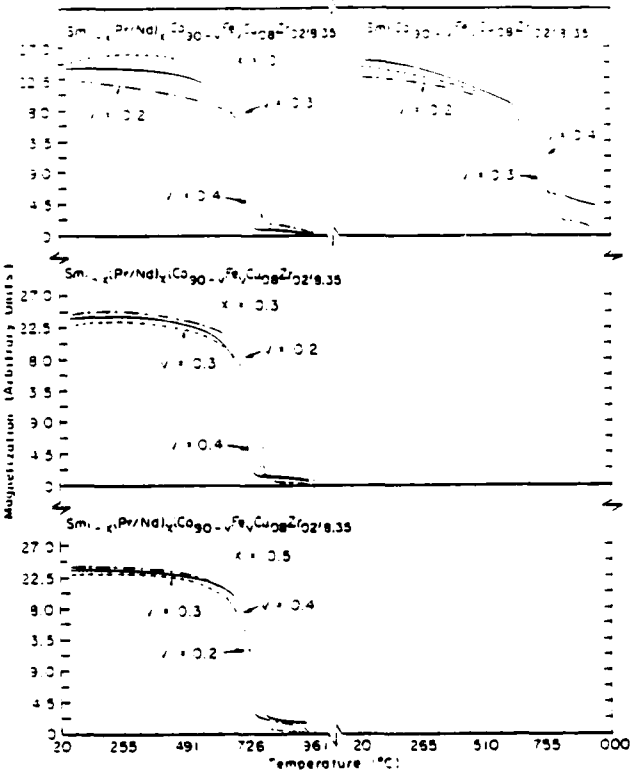


Figure 5. Temperature dependence of magnetization at an applied field of 1 kOe.

Table I. Base Alloy: $Sm_{1-x}(RE)_x(Co_{.90-v}Fe_vCu_{.08}Zr_{.02})_{8.35}$

Alloy	$_{18kG}$	M_S Extrapolated	B_S^2 - Theo. BH_{max} MGOe
x=0, y=0.2*	11,125	11,738	18.92
x=0, y=0.3*	10,872	11,550	16.66
x=0, y=0.4*	11,630	11,864	20.25
Pr, x=0.1, y=0.2*	11,229	11,888	19.12
Pr, x=0.1, y=0.3*	11,[illegible]	11,[illegible]	19.30
Pr, x=0.1, y=0.4*	11,356	11,[illegible]	18.81
Pr, x=0.3, y=0.2	11,342	11,589	18.29
Pr, x=0.3, y=0.3	11,241	11,576	18.28
Pr, x=0.3, y=0.4	10,468	10,725	14.79
Pr, x=0.5, y=0.2	11,911	12,225	20.48
Pr, x=0.5, y=0.3	11,728	12,025	19.41
Pr, x=0.5, y=0.4	10,179	10,544	13.92
Nd, x=0.1, y=0.2	11,046	11,213	16.71
Nd, x=0.1, y=0.3	10,726	10,919	14.88
Nd, x=0.1, y=0.4*	11,665	11,953	19.72
Nd, x=0.3, y=0.2	11,984	12,229	20.84
Nd, x=0.3, y=0.3	11,808	12,042	20.17
Nd, x=0.3, y=0.4	10,[illegible]	10,853	14.80
Nd, x=0.5, y=0.2	11,738	11,984	19.28
Nd, x=0.5, y=0.3	11,507	11,731	17.76
Nd, x=0.5, y=0.4	10,612	10,870	13.81
Pr/Nd, x=0.1, y=0.2	11,340	11,912	19.47
Pr/Nd, x=0.1, y=0.3	11,[illegible]8	11,602	19.70
Pr/Nd, x=0.1, y=0.4	10,984	11,270	15.56
Pr/Nd, x=0.3, y=0.2	11,305	11,[illegible]9	16.90
Pr/Nd, x=0.3, y=0.3	11,698	11,870	21.41
Pr/Nd, x=0.3, y=0.4	10,685	10,890	14.54
Pr/Nd, x=0.5, y=0.2	11,[illegible]8	11,900	19.91
Pr/Nd, x=0.5, y=0.3	11,366	11,[illegible]	[illegible].38
Pr/Nd, x=0.5, y=0.4	10,[illegible]3	10,[illegible]	13.[illegible]

*Measurement performed on non-homogenized sample.

best available copy.

The results indicate that Pr, Nd, or a combination of both can be effectively utilized for increasing the saturation induction and yet maintain reasonable values of anisotropy field. These alloys could be used for the fabrication of magnets. In an alloy containing x=0.3, a combination of Pr and Nd is more effective in maintaining the anisotropy field than either Nd or Pr alone. This effect may be related to subtle crystal field effects that changes the stabilization energy.

$Sm_{1-x}Pr_xCo_{30-y}Fe_yCu_{0.8}Zr_{0.2/8.35}$

	y = 0.2	y = 0.3	y = 0.4
x = 0	39	37	38
x = 0.1	38	38	5
x = 0.3	36	35	35
x = 0.5	49	39	25

$Sm_{1-x}Nd_xCo_{30-y}Fe_yCu_{0.8}Zr_{0.2/8.35}$

	y = 0.2	y = 0.3	y = 0.4
x = 0	39	37	38
x = 0.1	32	28	30
x = 0.3	34	33	37
x = 0.5	32	22	31

$Sm_{1-x}(Pr/Nd)_xCo_{30-y}Fe_yCu_{0.8}Zr_{0.2/8.35}$

	y = 0.2	y = 0.3	y = 0.4
x = 0	39	37	38
x = 0.1	34	37	35
x = 0.3	30	33	24
x = 0.5	39	29	24

Figure 6. Anisotropy field matrix for alloys studied.

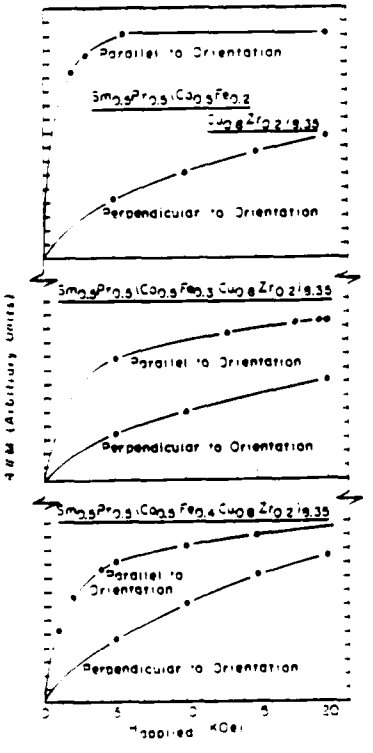


Figure 7. Typical magnetization vs H_A in easy and hard directions for one set of alloys.

CONCLUSION

The effect of Pr, Nd or a combination of Pr and Nd is to increase the saturation magnetization without adversely effecting the anisotropy field. A few of the compositions show promise for utilization as permanent magnets. The potential energy product of several of the alloys exceed 40 MGOe.

Acknowledgments

We want to thank Dr. J. C. Hurt and Mr. E. J. Dulis for their interest in this work.

This work was supported by a grant from Army Research Office Contract No. DAA629-83-C-007.

REFERENCES

1. T. Ojima, S. Tomizawa, T. Yoneyama and T. Hori, IEEE Trans. Mag., MAG-13, p. 1317 (1977).

2. R. K. Mishra, J. Thomas, T. Yoneyama, A. Fukuno and T. Ojima, J. Applied Physics, 52, p. 2517 (1981).

3. T. Shimoda, T. Okonogi, K. Kasai and K. Teraishi, IEEE Trans. Mag., MAG-16, p. 991 (1980).

4. A. E. Ray, H. F. Mildrum and J. B. Krupar, IEEE Trans. Magnetics, MAG-19, p. 2044 (1983).

5. (a) Y. Khan, Acta Cryst. 1329, p. 2503 (1973). (b) W. Ostertag and K. Strnat, Acta Cryst. 21, p. 560 (1966).

6. W. E. Wallace and K. S. V. L. Narasimhan, "Science and Technology of Rare Earths," p. 393-413, Academic Press, 1980; edited by E. C. Subbarao and W. E. Wallace.

7. K. S. V. L. Narasimhan, W. E. Wallace, R. D. Hutchens and J. E. Greedan, AIP Conf. Proc. 18, p. 1212 (1973).

The material contained in this paper is intended for general information only and should not be used in relation to any specific application without independent study and determination of its applicability and suitability for the intended application. Anyone making use of this material or relying thereon, assumes all risk and liability therefrom.

TO BE PUBLISHED

NdFeB MAGNETS WITH ZERO TEMPERATURE COEFFICIENT OF INDUCTION

Bao-Min Ma, K. S. V. L. Narasimhan*,
and J. C. Hurt**

*Crucible Materials Corporation
Crucible Research Center
P. O. Box 88, Pittsburgh, Pa. 15230

**U. S. Army Research Office
P. O. Box 12211
Research Triangle Park, N. C. 27709

ABSTRACT

Temperature compensation for the induction of NdFeB type magnets has been investigated. A computer assisted alloy selection method was adopted to identify composition of zero temperature coefficient of induction over -50 to 200°C. Selected alloys were processed into magnet by the conventional powder metallurgy method. The experimental temperature coefficient on the sintered magnet correlated with the prediction satisfactory. Holmium is an essential ingredient required for temperature compensation of NdFeB magnets. A magnet, $(Nd_{0.23}Ho_{0.64}Dy_{0.13})_{15}Fe_{79}B_6$ with B_r of 7,700 Gauss, H_c of 7,700 Oe, H_{ci} of 20,600 Oe, BH_{max} of 14.8 MGOe and temperature coefficient of -0.029% per °C over -50 to +150 was obtained.

INTRODUCTION

Neodymoum-iron-boron magnets have high energy product [1-3]. However, the temperature dependence of magnetic induction is about -0.08% to -0.12% per °C over -50 to 150°C. We have investigated heavy rare earth alloying to improve the temperature dependence. A computer assisted composition selection procedure developed for $SmCo_5$ and the 2:17 [4-7] alloys has been extended to NdFeB alloys.

In excess of 3000 alloy compositions were generated from the magnetization data of $Nd_2Fe_{14}B$ and $HRE_2Fe_{14}B$ alloys. The magnetization of $(NdHRE)_2Fe_{14}B$ was computed by adding the Nd and HRE moment linearly. The details are presented in this publication.

EXPERIMENTAL

A data base of the temperature dependence magnetization and anisotropy field of $Nd_2Fe_{14}B$ as well as $HRE_2Fe_{14}B_8$ (where HRE = Ho, Dy, Er, Tm and Tb) were constructed over -50°C to +250°C at 25°C intervals.

The substitution of heavy rare earth was assumed to replace the Nd sites. The magnetization of the combination of $NdHRE_2Fe_{14}B$ was calculated by adding the Nd and heavy rare earth moment linearly. The temperature coefficient α is defined as:

$$\alpha\ (\%\ \text{per}\ ^{o}C) = 100\% * [M(T_2)-M(T_1)]/[M(T_1)*(T_2-T_1)]$$

and calculated by a least square linear fitting. A Hewlett-Packard 85 computer with memory space of 32K was utilized to conduct these calculations.

Two criteria were set for the composition selection: (1) the selected composition must have a saturation magnetization greater than 7,500 Gauss at 25°C, and (2) the temperature coefficient of the induction must be less than -0.01% per °C over -50 to +200°C. The replacement of Nd with each individual heavy rare earth were scanned from 0 to 100% at 2% increments. Both the temperature dependence magnetization curve and temperature coefficient α were examined simultaneously. Neodymium mixed with two or three heavy rare earths were also examined at 2% increments respectively.

Selected alloy compositions were prepared by vacuum induction melting and cast into a copper mold. Ingots were processed into magnets by the traditional powder metallurgy method utilizing a process similar to that used for $SmCo_5$.

The temperature coefficient of induction, α, of the sintered magnets with length to diameter ratio (L/D) of 1.0-1.2 were measured by the open circuit technique (OCT) [8] from -50 to +150°C at 25°C intervals. The demagnetization curves of the sintered magnets were also measured by closed circuit technique (CCT) for the same temperature range.

The Curie temperature of the cast alloy or sintered magnet were measured by thermomagnetic analysis (TMA) under an applied field of 4 kOe. Samples were crushed to -400 mesh powder then sealed under inert atmosphere into a Vycor capsule for measurement.

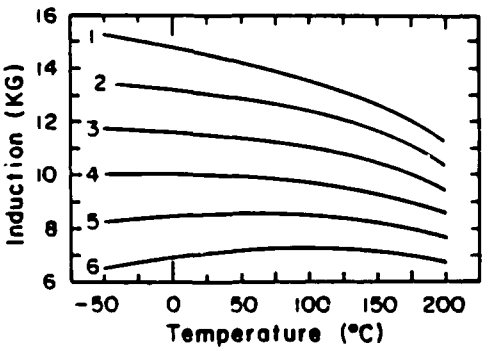
RESULTS AND DISCUSSION

Two of the $R_2Fe_{14}B$ alloys, $Dy_2Fe_{14}B$ and $Tb_2Fe_{14}B$, have temperature coefficient α less than -0.01 per °C as shown in Table I.

Table I. The Saturation Magnetization M_s at 25°C and Temperature Coefficient of Heavy Rare Earth $HRE_2Fe_{14}B$ Alloys

$R_2Fe_{14}B$ R=	M_s (Gauss)	Temperature Coefficient % per °C(-50 to +200)
Ho	7,060	+0.016
Tb	5,970	-0.007
Dy	6,160	+0.007
Gd	7,450	-0.053
Er	7,890	-0.042
Tm	9,810	-0.078

Owing to the higher magnetic moment of $Nd_2Fe_{14}B$, the combination of Nd with one of the heavy rare earth results in an increased magnetization. The slope of the overall curves can also be adjusted by varying the relative amount of Nd-HRE combination. Illustrated in Figure 1 are the temperature dependence magnetization curves of $(Nd_{1-x}Ho_x)2Fe_{14}B$, where x = 0 to 1.0 in steps of 0.2.



No.	$R_2Fe_{14}B$ % of R Nd	Ho
1	100	0
2	80	20
3	60	40
4	40	60
5	20	80
6	0	100

Figure 1. Computer simulated temperature dependence magnetization curves of $(Nd_{1-x}Ho_x)2Fe_{14}B$, where x = 0, .2, .4, .6, .8, and 1.0.

The combination of Nd with other single heavy rare earth were also examined for the entire composition range at 2% increments. Similarly, a combination of Nd with either two or three heavy rare earths were examined. Listed in Table II are the representative compositions of low temperature coefficient alloys with their saturation magnetization at 25°C.

Table II. The Saturation Magnetization at 25°C and the Temperature Coefficient of $R_2Fe_{14}B$ Type Magnet Generated by Computer Aid Alloy Composition Selection Method

% of Rare Earth in $R_2Fe_{14}B$							M_s(25)	Temperature Coefficient (% per °C)	
Nd	Ho	Dy	Gd	Er	Tm	Tb	(Gauss)	-50 to 150	-50 to 200
9	91						7800	+0.021	-0.006
8	85		7				7700	+0.018	-0.008
5	85				10		7710	+0.021	-0.008
10	55	35					7400	+0.015	-0.009
8	85			7			7720	+0.021	-0.007
6	85				9		7760	+0.020	-0.010
10	86					4	7770	+0.017	-0.008
10	72	16	2				7650	+0.015	-0.010
14	40	40	6				7710	-0.000	-0.021
8		38		52		2	7680	+0.001	-0.035
8	84			6	2		7770	+0.019	-0.009

Figures 2 and 3 show the computer simulated curves for various heavy rare earth containing $Nd_2Fe_{14}B$ alloys. From these curves, selected alloy compositions were processed into magnets. The properties of these low temperature coefficient magnets are listed in Table III.

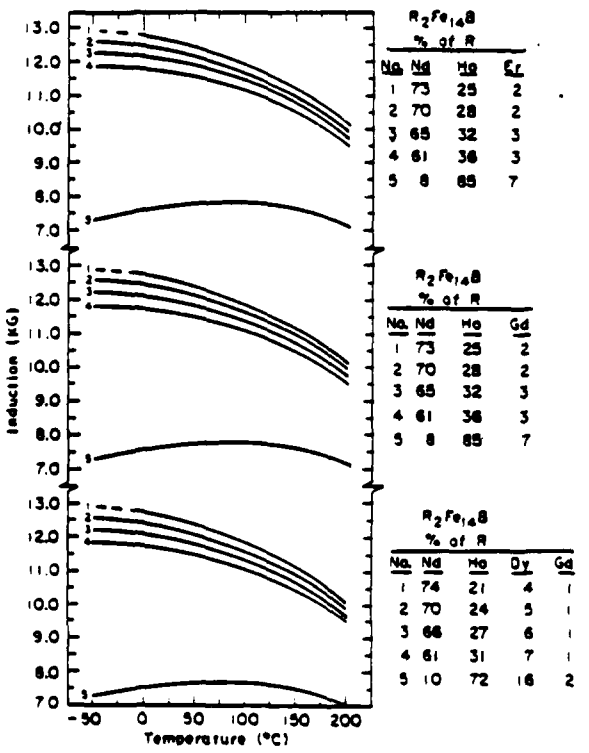


Figure 2. Computer simulated temperature dependence magnetization curves of $(NdHoEr)_2Fe_{14}B$, $(NdHoGd)_2Fe_{14}B$, and $(NdHoDyGd)_2Fe_{14}B$ on the corresponding sintered magnets with slightly higher Nd content.

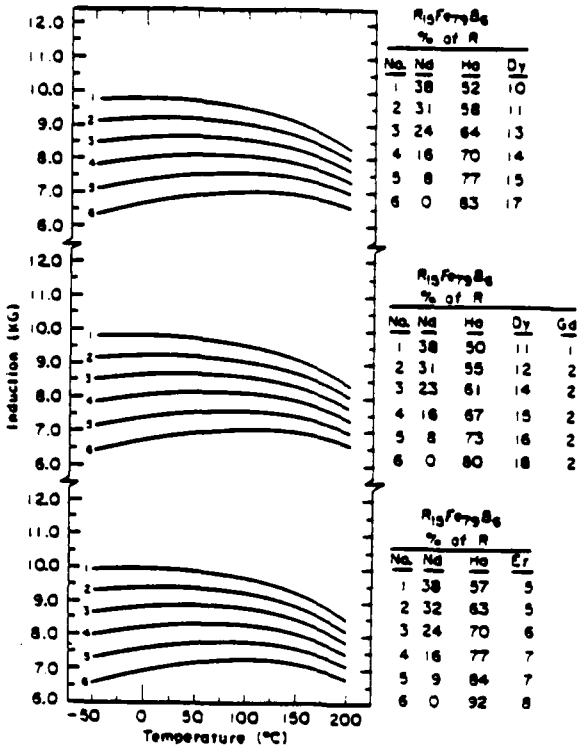


Figure 3. Computer simulated temperature dependence magnetization curves of $(NdHoDy)_2Fe_{14}B$, $(NdHoDyGd)_2Fe_{14}B$ and $(NdHoEr)_2Fe_{14}B$ of the corresponding low temperature coefficient sintered magnets.

Table III. Magnetic Properties of Temperature Compensated $R_2Fe_{14}B$ Type Magnet

	% of R in $R_2Fe_{14}B$					B_R	H_C	H_{CI}	BH_{MAX}	H_K	Density
No	Ho	Dy	Er	Tm	Gd	(Gauss)	(Oe)	(Oe)	(MGOe)	(Oe)	(gm/cc)
65	35	-	-	-	-	9,800	9,400	16,450	22.8	14,400	7.35
60	36	-	-	4	-	8,800	7,700	11,950	16.8	6,400	7.06
61	36	-	3	-	-	8,900	8,800	14,900	20.3	10,500	7.24
32	63	-	5	-	-	7,900	7,700	14,400	15.2	13,000	7.80
65	32	-	-	-	3	8,900	7,750	10,850	17.6	8,700	7.11
61	31	7	-	-	1	9,350	9,000	20,470	20.3	19,850	7.44
24	64	12	-	-	-	7,700	7,700	20,600	14.8	18,300	7.98

Two magnets with the nominal composition of $(Nd_{0.24}Ho_{0.70}Er_{0.06})_{15}Fe_{79}B_6$, magnet A, and $(Nd_{0.23}Ho_{0.64}Dy_{0.13})_{15}Fe_{79}B_6$, magnet B, were selected for (1) the closed circuit temperature dependence demagnetization curve measurement and (2) the open circuit temperature dependence of induction measurements. Figures 4 and 5 are the temperature dependence demagnetization curves of these two magnets. The temperature dependence magnetic properties of these two magnets are summarized in Figure 6a and 6b respectively. In figures 7 and 8, the temperature dependence magnetization curves of magnet A and B are normalized to their values of -50°C. Shapes of the

Shapes of the computer generated curves and the experimental curves favorably compare. The temperature coefficients are tabulated in Table IV. The other two magnets with higher Nd contents are also listed for comparison.

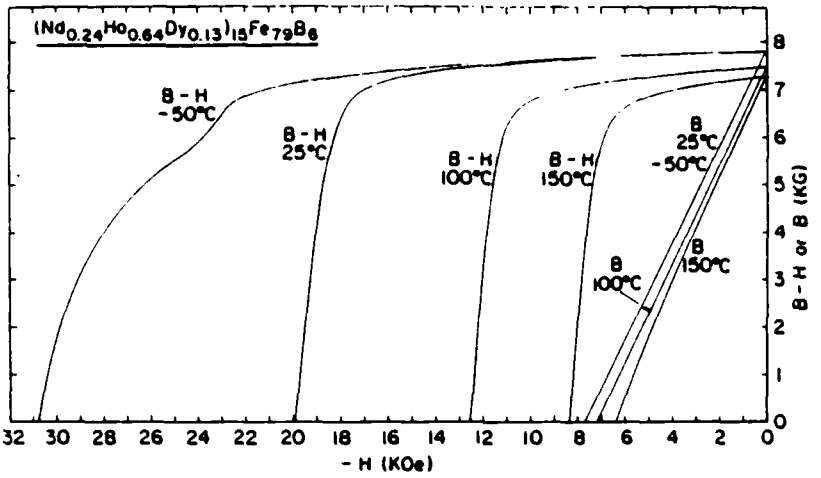


Figure 4. The temperature dependence demagnetization curves of $(Nd_{0.23}Ho_{0.70}Dy_{0.13})_{15}Fe_{79}B_6$.

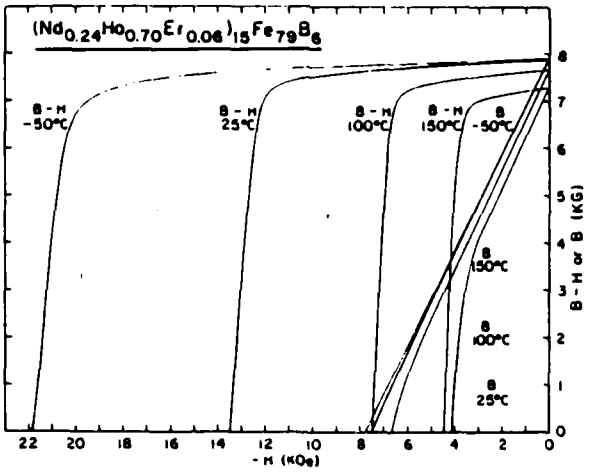


Figure 5. The temperature dependence demagnetization curves of $(Nd_{0.24}Ho_{0.70}Er_{0.06})_{15}Fe_{79}B_6$.

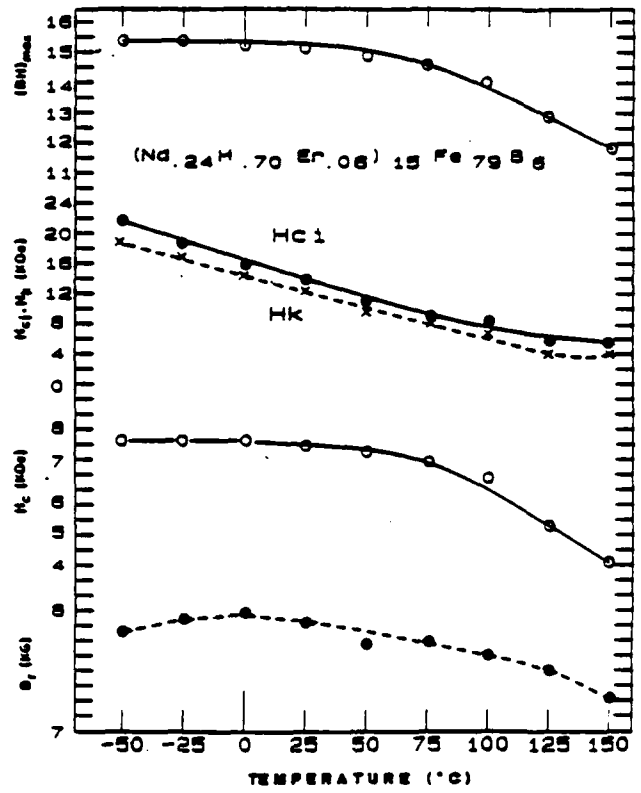


Figure 6a. The temperature dependence magnetic properties of Magnet A.

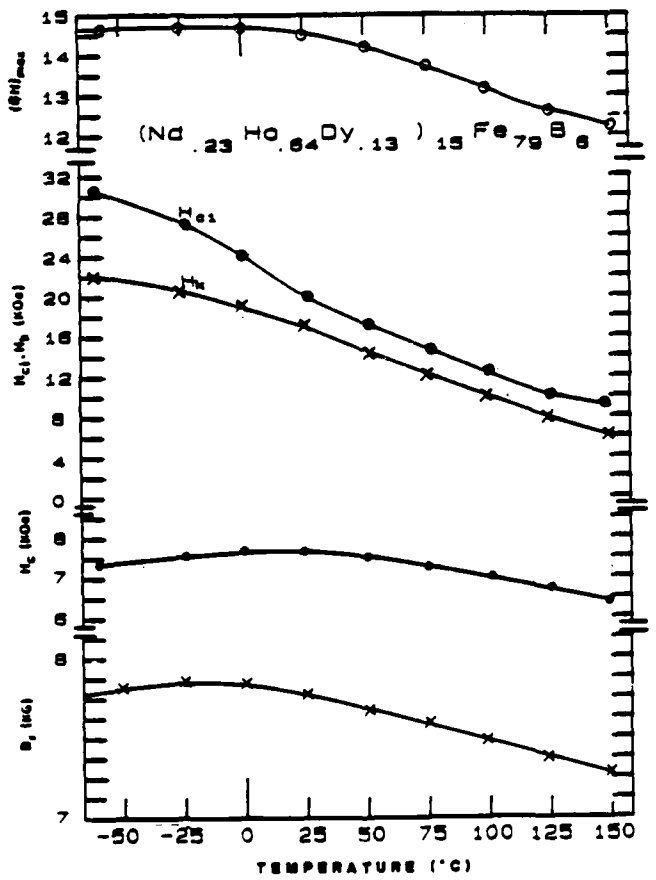


Figure 6b. The temperature dependence magnetic properties of Magnet B.

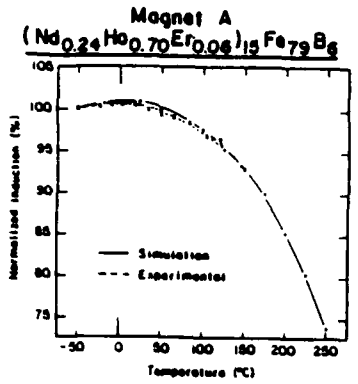


Figure 7

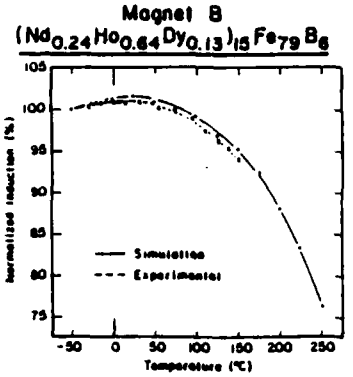


Figure 8

Figure 7. The experimental and computer simulated temperature dependence magnetization of Magnet A normalized to their values of -50°C.

Figure 8. The experimental and computer simulated temperature dependence magnetization of Magnet B normalized to their values of -50°C.

Table IV. The Comparison of the Temperature Coefficient α of the Experimental Results with Computer Simulated Results

Magnet	% of R in $R_{15}Fe_{79}B_6$					Temperature Coefficient α % per °C (-50 to +150)	
	Nd	Ho	Dy	Er	Gd	experimental	simulation
A	24	70		6		-0.034	-0.013
B	23	64	13			-0.029	-0.012
C	61	31	7		1	-0.070	-0.061
D	65	35				-0.074	-0.063

We have extended the computer technique for the computation of anisotropy field utilizing anisotropy field variation with temperature of $Nd_2Fe_{14}B$ and $(HRE)_2Fe_{14}B$ alloys. The room temperature anisotropy field compare within 5 kOe of the computed fields.

CONCLUSION

Computer simulation technique employed produced alloy compositions that compare favorably with experimental observation on sintered magnets. Number of alloys with varying levels of temperature compensation are available from the rare earth-iron-boron alloys.

ACKNOWLEDGEMENT

We thank Mr. E. J. Dulis for his interest in this work and the technical assistance of Mr. T. W. Sloan is appreciated.

REFERENCES

1. K. S. V. L. Narasimhan, J. Appl. Phys. 57, 4081, (1985).

2. M. Sagawa, S. Fujimura, N. Togawa, H. Yamamoto and Y. Matsuura, J. Appl. Phys. 55, 2083, (1984).

3. R. W. Lee, E. G. Brewer and N. A. Schaffel, IEEE Trans. Magn., MAG-21, 1958, (1985).

4. M. G. Benz, R. P. Lorfce and D. L. Martin, AIP Conf. Proc., No. 18, 1173, (1974).

5. K. S. V. L. Narasimhan, Proc. Fifth International Workshop on Rare Earth Cobalt Permanent Magnets and Their Applications, Roanoke, Va., June 1981, University of Dayton, p. 629 (1981).

6. H. A. Leupold, E. Potenziani, A. Tauber, and H. F. Mildrum, J. Appl. Phys. 55, 2097, (1984).

7. F. E. Camp and K. S. V. L. Narasimhan, IEEE Trans. Magn., MAG-21, 1970, (1985).

8. K. Sagawa, S. Fujimura, H. Yamamoto, Y. Matsuura, S. Hirosawa, and K. Hiraga, Proc. 8th International Workshop on Rare Earth Magnets and Applications, Ed. by K. J. Strnat, University of Dayton, p. 587 (1985).

FIGURES

1. Computer simulated temperature dependence magnetization curves of $(Nd_{1-x}Ho_x)_2Fe_{14}B$, where x = 0, .2, .4, .6, .8, and 1.0.

2. Computer simulated temperature dependence magnetization curves of $(NdHoEr)_2Fe_{14}B$, $(NdHoGd)_2Fe_{14}B$, and $(NdHoDyGd)_2Fe_{14}B$ on the corresponding sintered magnets with slightly higher Nd content.

3. Computer simulated temperature dependence magnetization curves of $(NdHoDy)_2Fe_{14}B$, $(NdHoDyGd)_2Fe_{14}B$ and $(NdHoEr)_2Fe_{14}B$ of the corresponding low temperature coefficient sintered magnets.

4. The temperature dependence demagnetization curves of $(Nd_{0.23}Ho_{0.70}Dy_{0.13})_{15}Fe_{79}B_6$.

5. The temperature dependence demagnetization curves of $(Nd_{0.24}Ho_{0.70}Er_{0.06})_{15}Fe_{79}B_6$.

6a. The temperature dependence magnetic properties of Magnet A.

6b. The temperature dependence magnetic properties of Magnet B.

7. The experimental and computer simulated temperature dependence magnetization of Magnet A normalized to their values of -50°C.

8. The experimental and computer simulated temperature dependence magnetization of Magnet B normalized to their values of -50°C.

END

DTIC

8-86